DYNAMICS OF OXIDATION-REDUCTION PROCESSES IN RARE-EARTH-DOPED CaF_2

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The effects of high-energy radiation on single crystals of alkaline halides have been studied in great detail, and a number of color centers have been identified in these systems.[1] The corresponding situation in the alkaline earth fluorides is much more complex.[2] The latest evidence indicates that all coloration in CaF_2 is associated with impurities, and very pure crystals are not noticeably affected by γ irradiation.[3] We have studied the oxidation-reduction processes associated with rare-earth-doped CaF_2 crystals subjected to γ irradiation. Under the influence of high-energy radiation, some of the trivalent rare earths (RE^{3+}) convert to the divalent state (RE^{2+}),[4,5] leaving an unidentified hole behind. The divalent rare earth produced is not stable; it reoxidizes to the trivalent state accompanied by luminescence characteristic of the trivalent rare earth.

In this note we wish to report on the mechanism of this reconversion, triggered either by heat or by infrared radiation. The reoxidation is accompanied by both luminescence and photoconductivity,[6] and the excitation spectra of the two phenomena are identical. The luminescence spectrum is characteristic of the trivalent rare-earth ion in a cubic environment. The IR-triggered reconversion rate is faster than 10^{-6} sec.

To study the thermoluminescence, single crystals of CaF_2 containing trivalent rare earth of 0.02-1.0 molar percent were irradiated at 78°K using γ irradiation from a spent reactor fuel rod and dosages of the order of 10^6 rad. The RE^{2+} concentration was monitored by recording the $4f$-$5d$ absorption bands[5] of the ions. The crystals were warmed to room temperature, while the luminescence spectra were photographed with a Bausch and Lomb 2-m grating spectrograph having an effective resolution of 1 cm^{-1}. All the rare-earth-doped samples were found to emit some radiation, but only the Dy and Tm systems were investigated in detail.

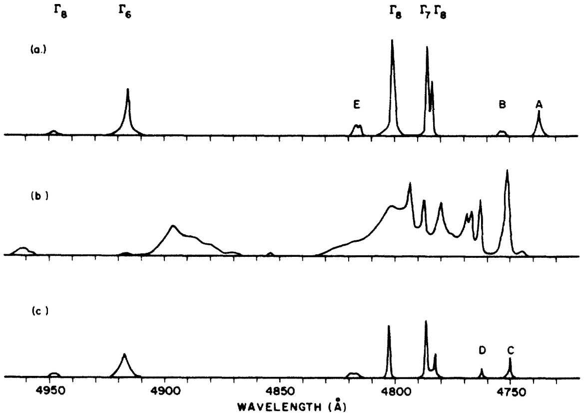

FIG. 1. (a) Thermoluminescence spectrum of 0.1 mole % CaF_2:Dy, γ-irradiated at 78°K and warmed to 300°K. The transition is between ${}^6F_{11/2} \rightarrow {}^6H_{15/2}$ states of Dy^{3+}. (b) Fluorescence spectrum of 0.1 mole % CaF_2:Dy^{3+} before γ irradiation at 78°K. (c) Luminescence spectrum of CaF_2:Dy at 78°K when the crystal is excited with light of longer wavelength ($\lambda_{exc} > 5000$ Å) than the emission lines ($\lambda_E = 4900$ Å). The crystal was irradiated with γ rays at 78°K and was kept at this temperature. (The line, A, is emission from the excited thermalized state of ${}^6F_{11/2}$. B and E are possible vibronic compounds. C and D are some "noncubic" lines excited.)

Figure 1(a) shows a densitometer trace of a photograph of the thermoluminescence spectrum accompanying the Dy^{2+}-Dy^{3+} conversion. The lines correspond to the ${}^6F_{11/2} \rightarrow {}^6H_{15/2}$ transition of Dy^{3+}.[7] Figure 1(b) shows a fluorescence spectrum of the crystal before irradiation. While the two spectra cover the same frequency range and originate from the same groups of transitions, we suggest that the simpler thermoluminescence spectrum of Fig. 1(a) is characteristic of Dy^{3+} in a cubic site. The evidence for this suggestion is as follows: (1) While the fluorescence spectrum of Dy^{3+} is strongly concentration dependent, the thermoluminescence spectrum is concentration independent. (2) The positions of the five crystal-field components of the ${}^6H_{15/2}$ level (indicated by symbols Γ_i) as deduced from Fig. 1(a) can be well fitted by a cubic field description.[8] (3) The first excited crystal-field level of the ground state Γ_7 is 8.3 cm^{-1} above the ground Γ_8 level [Fig. 1(a)], and this level has been observed in paramagnetic resonance,[9] and identified as originating from Dy^{3+} in cubic sites. We conclude that the luminescing Dy ion is undergoing the Dy^{2+}-Dy^{3+} reconversion process. This is corroborated by previous observations that γ irradiation only reduces RE^{3+} ions in a cubic site,[10] and that RE^{2+} ions remain in a cubic site.[5]

We have found that the RE^{2+} can be reconverted to RE^{3+} with visible and infrared radiation, and that this photo-oxidation process is accompanied by the same cubic-site RE^{3+} emission as found in the thermoluminescence [Fig. 1(c)]. The system behaves as an IR-stimulable phosphor, where, for example [Fig. 1(c)], the 4900Å emission can be triggered by IR photons (up to $\lambda \leq 9000$ Å). The excitation spectrum of a trivalent thulium luminescence is shown in Fig. 2(b). The spectrum was taken by monitoring the intensity of the 4500Å emission line of Tm^{3+}, corresponding to the transition ${}^1G_4 \rightarrow {}^3H_6$, while the crystal was excited through a second monochromator using a tungsten lamp. The absorption spectrum of the same crystal is shown on Fig. 2(a), showing the characteristic $4f$-$5d$ bands of CaF_2:Tm^{2+}.[5] While the peaks of the Tm^{3+} excitation spectrum of Fig. 2(c) occur at the same wavelength as the $5d$ bands of Tm^{2+}, it increases very rapidly with increasing frequency. The crystals are also photoconducting while irradiated with IR light,[6] and the frequency response of the photoconductivity is shown in Fig. 2(b). It can be noted that the excitation spectrum of the Tm^{3+} luminescence reflects closely the photoconductive response curves.

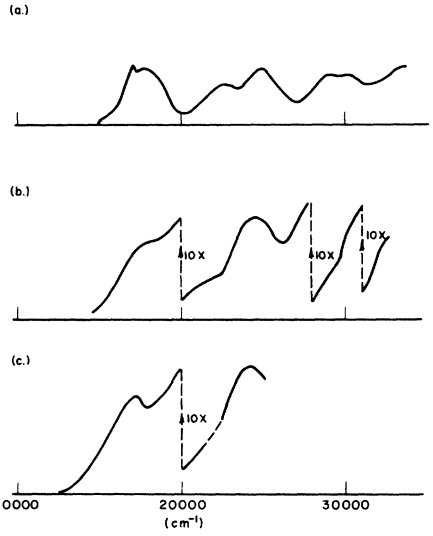

FIG. 2. (a) The absorption spectrum of CaF_2:Tm irradiated with γ rays at 78°K. (b) The photoconductivity response of CaF_2:Tm^{2+} as a function of excitation frequency. (c) The excitation spectrum of the 4500Å Tm^{3+} emission when the γ-irradiated crystal is excited with the light $\lambda_{exc} > 4500$ Å.

In an attempt to measure the rate of photo-oxidation, we have recorded the time dependence of the 4900Å Dy^{3+} emission, after the crystal was excited with a light pulse of 3-μsec duration and having wavelengths longer than 5000 Å. The Dy^{3+} emission showed no resolvable rise time, indicating that the reconversion rate is faster than the time resolution of the instrument, which was 10^{-6} sec. The luminescence then decays in two steps. First there is a fast, exponential decay measurable for about 50 msec, having a lifetime of $\tau = 1.9$ msec at 78°K. This is the right order of magnitude for the lifetime of a magnetic-dipole transition which would be expected between states of Dy^{3+} in cubic site. Following this fast exponential decay, there is luminescence of much lower intensity which persists for minutes, and has a complex time dependence. The number of photons emitted during the short exponential decay is of the same order of magnitude as the total number of photons emitted during the much weaker but longer persistent luminescence.

We cannot yet fit all the observations on the oxidation-reduction processes into a consistent picture, but the above observations elucidate points not previously understood. From previous observations,[10] we know that γ radiation converts only RE^{3+} in a cubic site to RE^{2+}. This presumably occurs by taking an electron from an interstitial charge compensator F^-, which is distant from the RE^{3+} by more than a few lattice sites. We now suggest that the F^0 left behind is not stable and may combine with a second F^0 to form nonparamagnetic F_2 molecular complexes as the stable hole. Each RE^{2+} is in a cubic site, and it will remain RE^{2+} until one of two mechanisms triggers the reconversion: (1) The absorption of a photon lifts one of the RE^{2+} electrons into the conduction band. This conduction electron is trapped by an electron trap, presumably the hole created by γ irradiation, thus leaving a RE^{3+} excited ion in the cubic site which returns to the ground state by the observed characteristic cubic-site fluorescence. (2) The reconversion is triggered by thermal energy freeing the trapped hole. As this trapped hole approaches a RE^{2+}, it will capture one of the electrons of RE^{2+}, leaving again an excited RE^{3+} ion. Whether the mechanism of this trapping is by tunneling or by some other process is not yet known.

The existence of the F_2 molecule as the hole would qualitatively explain the time dependence of the IR-triggered luminescence. First the IR photons will free the electron, leading to photoconductivity. This electron is trapped by the F_2, breaks up the molecular complex, leaving an interstitial F^- charge compensator and a nonstable F^0. The second long part of the luminescence could correspond to the capture by this F^0 of one of the electrons of the RE^{2+}. This is in qualitative agreement with the observation that the number of photons emitted during the "slow" process is the same order of magnitude as during the "fast" process.

In summary, we have found that the luminescence associated with the reconversion of $RE^{2+} \rightarrow RE^{3+}$ in CaF_2 is characteristic of RE^{2+} ions in a cubic site. We would like to emphasize the importance and the ease of this technique for studies of the cubic RE^{3+} spectra in the fluoride hosts. This study is very difficult by the ordinary absorption and emission techniques, since it is always overlapped by a much more intense concentration-dependent noncubic spectrum. The RE^{2+} can be photo-oxidized, and the process leads to photoconductivity. The photo-oxidized reconversion triggers luminescence with two different time dependences. We wish to point out the possibility of laser action in the RE^{3+} emission associated with the $RE^{2+} \rightarrow RE^{3+}$ reconversion process.

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RELATIVISTIC ENERGY BANDS FOR TUNGSTEN*

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In this Letter the results of an ab initio relativistic calculation of the electronic structure of tungsten are presented. The predicted splitting of the energy bands is in complete agreement with the experimental results obtained from size effect measurements.[1]

The method used in these calculations was developed by the author and has recently been submitted for publication.[2] It can be thought of as a relativistic generalization of the augmented plane wave (APW) method of Slater.[3] The basic function consists of a Dirac plane wave in the outer region of the unit cell and an expansion of Dirac central-field orbitals inside the APW sphere. The expansion coefficients are chosen such that the upper (large) components of the wave function are continuous on the sphere. The lower (small) components are, in general, discontinuous on this surface. A variational expression, which is appropriate for this type of trial function, is developed. The resulting matrix elements have the following form:

$$M\binom{NM}{nm} = (k_N^2 - E)\Omega_{nN}\delta_{mM} + 4\pi R^2 \sum_\kappa D_\kappa \binom{NM}{nm} j_l(k_n R) \left\{ j_l(k_N R)\left(\frac{cf_\kappa(R,E)}{g_\kappa(R,E)}\right) - j_l(k_N R) k_N S_\kappa \right\}, \tag{1}$$

where

$$\Omega_{nN} = \Omega\delta_{nN} - 4\pi R^2 \frac{j_1(|\vec{k}_N - \vec{k}_n| R)}{|\vec{k}_N - \vec{k}_n|}, \tag{2}$$